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## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Process for the production of Finely Dispersed Calcium Carbonate

- We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of 22c, Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- Calcium carbonate precipitated from an aqueous solution has been used as a filler, particularly in the rubber industry, for a long time. In order to attain a reinforcing effect in the rubber, the filler should be extremely fine-particled while still readily dispersible. Commercial calcium carbonate caoutchouc fillers show specific surface (BET) values between 20 and 35m<sup>2</sup>/g (determined by the method of Brunnauer, Emmett and Teller). Electron microscope photographs show that such powders consist of almost cubic small crystals part of which have conglomerated to form secondary agglomerates. In general, the tendency to agglomerate is the greater, the finer the primary particles. The packing of the latter in the agglomerates may become so dense as to render grinding and dispersing difficult. The density of packing or, inversely, the degree of loosening may be characterised by the bulk weight, the settling volume and the oil adsorption. Particularly the oil adsorption or "oil number," that is the amount of linseed oil taken up by 1 g. of the powder until all particles are just completely wetted, gives an indication as to the obtainable particle surface and secondary structure, and may be determined according to Gardner, see "Physical and Chemical Examinations of Paints, Varnish, Lacquers and Colors," Gardner-Sward, Washington 1950, 11th Edn., page 290.
- The object of the invention is a process for the production of finely dispersed precipitated calcium carbonate with a disturbed calcite lattice and a loose secondary particle structure, and containing silicic acid in an amount corresponding to an SiO<sub>2</sub> content of 0.1 to 20%, preferably 0.5 to 10%, by weight based on CaCO<sub>3</sub>. The process according to the invention is characterised by reacting aqueous calcium-hydroxide suspension of not more than 1.0 molar concentration, at a starting temperature of 10° C. to 30° C., with carbon dioxide in the presence of an added aqueous alkali metal silicate solution or of an added freshly prepared silicic acid solution, the latter containing SiO<sub>2</sub> ions in a low polymerized state and having an SiO<sub>2</sub> content of not more than 10% by weight, and interrupting the supply of carbon dioxide to the suspension upon reaching a pH value of from 8.5 to 11 therein. The silicic acid solution is expediently prepared by diluting a water-glass solution to the aforesaid SiO<sub>2</sub> content, or by acidifying a dilute water-glass solution, or by treating a silicate solution with H<sup>+</sup>-exchange resin. Economically it is particularly advantageous to add silicate solutions, preferably commercial sodium silicate (Na<sub>2</sub>O.3.3SiO<sub>2</sub>) in a quantity corresponding to 0.1—20% by weight of SiO<sub>2</sub>, preferably 0.5—10% by weight of SiO<sub>2</sub>, referred to CaCO<sub>3</sub>, to milk of lime. It can be assumed that in the course of the carbonation process there is formed from the silicate a reactive silicic acid which apparently impairs the crystal growth of the CaCO<sub>3</sub>, as can be seen from the X-ray diffraction pattern. In contrast to other known mixed precipitations of non-isomorphous substances however, there is formed not a simple mixture of finely divided CaCO<sub>3</sub> and finely divided silicic acid, but, surprisingly, a novel homogeneous filler. It can be concluded from the electron microscope picture that the silicic acid surrounds the CaCO<sub>3</sub> crystals to a large extent. Even small additions of silicic acid of the order of 1% by weight of SiO<sub>2</sub>, referred to CaCO<sub>3</sub>, and added in the form of sodium

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silicate, substantially influence the properties of the filler thus formed.

The process proves to be particularly suitable for the manufacture of extremely finely divided calcium carbonate fillers. For this purpose it is expedient to carry out the reaction of the present invention with dilute carbonic acid containing 10 to 50% by volume of  $\text{CO}_2$ , advantageously 10—20% by volume of  $\text{CO}_2$ , and providing for the precipitation a constant excess of  $\text{CO}_2$ .

When the precipitation starts, the sodium silicate solution is added with intense stirring to the milk of lime the  $\text{Ca}(\text{OH})_2$  concentration of which is kept at or below 1 molar. In this manner,  $\text{CaCO}_3$  fillers with specific surfaces of more than 50  $\text{m}^2/\text{g}$  are obtainable which, although finely divided, are readily dispersible. An explanation for the surprisingly good dispersibility is supplied by the electron microscope picture. The almost spherical  $\text{CaCO}_3$  particles form loose grape-like secondary agglomerates such as are typical of silicic acid fillers, but have not hitherto been known for  $\text{CaCO}_3$  fillers. The silicic acid filler-like properties are also apparent in that the precipitate can be flocculated by cation-active additives, a typical feature of silicic acid. This property can be utilised with advantage for filtration, for example by concentrating the precipitate before filtering.

If in addition to active silicic acid nitrotri-acetic acid is added to the milk of lime in quantities of 0.01—0.5%, in the form of one of its water-soluble salts, expediently in the form of the sodium salt, the process of the invention yields  $\text{CaCO}_3$  particles of changed appearance, i.e., oblong spherical particles which tend to aggregate in the form of little rods (see our co-pending Application No. 34693/60) (Serial No. 903,345). In this way there are obtained under suitable precipitating conditions either fillers of even finer particle size or, if secondary aggregates in the form of little rods are formed, extremely voluminous products on account of the especially loose and bulky packing.

With regard to their reinforcing effect on rubber elastomers the silicic acid-containing calcium carbonate fillers according to the invention may still be improved after precipitation by heating the aqueous suspension at an alkaline pH value up to 10 to temperatures above 70° C., preferably to boiling temperature. The silicic acid present on the  $\text{CaCO}_3$  particles is stabilised by heating in a weakly alkaline medium. The initial porosity of the extremely finely divided amorphous silicic acid layer is reduced, and this becomes manifest in a more or less substantial decrease of the BET value, depending on the content of silicic acid. It is noteworthy that in this case a growth of the  $\text{CaCO}_3$  crystallites does not occur, whilst precipitation at temperatures above 70° C yields coarse-grained  $\text{CaCO}_3$ .

With regard to the reinforcing effect on elastomers the silicic acid-containing calcium carbonate fillers according to the invention are superior to those hitherto known.

According to the present invention, the reaction between the calcium hydroxide suspension and the carbon dioxide is stopped when the pH value of the suspension (which is above 12 at the start) reaches a value of between 11 and 8.5. In this way there are obtained in a reproducible manner, silicic acid-modified  $\text{CaCO}_3$  fillers with high BET values of 50—100  $\text{m}^2/\text{g}$ , a loose secondary structure, and thus a good grinding capability and dispersibility. Carbonation is preferably carried out down to a pH of from 9 to 10. If the reaction were to be continued at pH values below 8, this would lead to products of substantially harder agglomeration. This knowledge stands in contrast to the understandable desire to carbonate the  $\text{Ca}(\text{OH})_2$  completely, in order to obtain a calcium carbonate at neutral as possible.

As in the case with every neutralisation reaction, the pH value of the suspension falls from that of  $\text{Ca}(\text{OH})_2$ , i.e., above 12, only towards the end of the reaction within a relatively short time so that a precise pH control is advisable, in order to stop the reaction in time. After stopping the  $\text{CO}_2$ -containing gas stream, the pH value rises in most cases upon further stirring by several tenths, since enclosed  $\text{Ca}(\text{OH})_2$  dissolves. In order to attain the desired final pH value, this rise may be taken into account from the start or an after-carbonation may be carried out for a short time. The falling of the pH value in the final phase of carbonation proceeds the less rapidly, the greater the quantity of silicic acid present.

The dependency of the properties of the  $\text{CaCO}_3$  filler on the final pH value of the reaction can already be recognised during filtration. The higher the water content of the filter cake or the lower the dry contents of the filter cake, the looser the secondary structure, equal size of primary particles or equal specific surface being presupposed. At below pH 8 the dry contents of the filter cake rises strongly, i.e., the particles are more densely packed and dry to form harder agglomerates. An explanation for these observations is supplied by the analytical composition of the final products. In  $\text{SiO}_2$ -containing  $\text{CaCO}_3$  fillers which are reacted only down to a pH value of 8.5—11 there is found, in addition to the resulting  $\text{CaCO}_3$ , a  $\text{CaO}$  excess approximately corresponding to the  $\text{SiO}_2$ -content in the form of a calcium silicate. It can be assumed that the silicic acid in the form of a calcium hydroxo-silicate causes a linkage of the  $\text{CaCO}_3$  particles to form loose aggregates. Upon further carbonation this linkage is destroyed to a large extent with the formation of further  $\text{CaCO}_3$ , the filter cake becomes more dense and binds less water and shrinks upon drying

to form harder agglomerates which are ground less easily.

In addition to the pH value, there was found another influence on the secondary structure, i.e., shearing stress in the precipitation. In order to achieve the desired aim to obtain primary particles as fine as possible and having a loose secondary structure, the CO<sub>2</sub>-containing gas must be finely divided for the purpose of a rapid reaction, but with a shearing effect as low as possible. Particularly advantageous are rapidly rotating gassing stirrers in which the gas is conducted through the hollow stirrer shaft and leaves through apertures at the circumference of the stirrer. Stirrers of this type are described for example in German Patent Specification No. 1,032,719. The precipitating container itself is expediently fitted with radial wave breakers having a width of about 1/10 of the diameter of the container (see "Chemie-Ingenieur-Technik" 31, 9 (1959), page 588 ff). Other conditions of precipitation being equal, such gassing stirrers yield lower dry contents of the filter cake and more voluminous products than the rapidly rotating turbine stirrers, not to mention the strongly shearing stirrers provided with a stator basket.

The following Examples are given for the purpose of illustrating the invention.

#### EXAMPLE 1.

To 200 litres of a 0.6 molar milk of lime there are added with stirring 1.43 litres of an aqueous solution of sodium silicate, containing 1.7 mol per litre of Na<sub>2</sub>O. 3.3 SiO<sub>2</sub>, corresponding to a SiO<sub>2</sub>-addition of 4 per cent by weight, calculated upon the calcium carbonate. The milk of lime has a temperature of 17° C. A gas stream, consisting of a mixture of 5 m<sup>3</sup> carbon dioxide and 20 m<sup>3</sup> air per hour is introduced with stirring by a turbostirrer. After 38 minutes the temperature rises to 33° C and the p<sub>H</sub>-value has diminished to 9.35. The current of gas is stopped. The complex calcium-carbonate-silicate is filtered off, dried and ground in a pin-mill. The finely divided, lightly dispersible filler has a specific surface area according to BET of 79 m<sup>2</sup>/g, a sedimentation volume (2 g of the filler agitated in 98 g of toluene) of 31 cm<sup>3</sup> and an oil adsorption of 0.83 ml/g.

The X-ray diffraction pattern shows that the calcite structure is strongly disturbed.

#### EXAMPLE 2.

To 12 litres of a 0.6 molar milk of lime there are added with stirring 105 ml of an aqueous solution of sodium silicate contain-

ing Na<sub>2</sub>O. 3.3 SiO<sub>2</sub> corresponding to a SiO<sub>2</sub>-addition of 6 per cent by weight of calcium carbonate. A gas stream of 2500 litres per hour, containing carbon dioxide in an amount of 20 per cent by volume, is introduced with stirring at a starting temperature of 15° C. After 23 minutes the current of gas is stopped. The temperature rises to 34° C and the p<sub>H</sub>-value has diminished to 9.2. The complex calcium-carbonate-silicate is filtered off. The content of solid material of the filter cake amounts to 24 per cent by weight. After drying and grinding, the filler shows a specific surface area according to BET of 82 m<sup>2</sup>/g and sedimentation volume of 26 cm<sup>3</sup>. (Oil adsorption value of 0.85 ml/g).

#### EXAMPLE 3.

Into a cylindrical 20 litres container fitted with 4 radial wave breakers having a width of 1/10 of the diameter, there are placed 15 litres of 0.5 molar milk of lime. A quadrangular gassing stirrer having an edge length of 43 mm corresponding to 60 mm diameter in the diagonal and a height of 100 mm (according to German patent specification No. 1,032,719) serves for the distribution of the gas mixed from 20% by volume of CO<sub>2</sub> and 80% by volume of air. The stirrer rotates in the centre of the vessel about 80 mm above the bottom at about 2000 r.p.m. This speed of rotation is sufficient for distributing the gas stream of 2500 litres per hour conducted through the hollow axle and leaving through slots at the stirrer edges, evenly throughout the whole volume of liquid.

To the milk of lime, 6% by weight SiO<sub>2</sub> referred to CaCO<sub>3</sub> is added in the form of silicic brine of pH 3 freshly prepared from dilute silicate solution (Na<sub>2</sub>O. 3.3 SiO<sub>2</sub>) and hydrochloric acid. Subsequently the gas stream is introduced at an initial temperature of 18° C. In a first experiment carbonation is carried out up to pH 11 and the resulting calcium carbonate filtered, washed, dried and ground. In further experiments, the process is carried out correspondingly, but the reaction continued to final pH values of 10; 9; 8.5; 8 and 7.1. Analysis of the resulting fillers shows for final pH values between 11 and 8, in addition to CaCO<sub>3</sub>, a content of hydrated calcium silicate of the approximate formula CaO.(SiO<sub>2</sub>)<sub>1-2</sub>.nH<sub>2</sub>O. The filler obtained by reacting until pH 7 contains only hydrated silicic acid in addition to CaCO<sub>3</sub>. The properties of the fillers, otherwise prepared in equal manner, as a function of the final pH value are given in the following Table.

final pH	carbonisation time	dry cont. of filter cake in % by weight	settling volume in cc	specific surface accord. to BET in m <sup>2</sup> /g.
11	27	20	32	83
10	29	19	38	95
9	31	18	39	96
8.5	31.5	21	37	82
8	33	22	27	75
7.1	36	34	15	68

It can be seen that the properties of the filler fall off at about pH 8 and are unfavourable at pH 7.1. The settling volume (2 g of filler shaken in 98 g of toluene and the settling volume read after standing for an hour) amounts only to 15 cc, the BET value is lower than at higher pH values; the dry contents of the filter cake is substantially higher, corresponding to the denser packing of the particles. The most advantageous values are obtained in products carbonated to a pH value of about 9—10. They are especially loose and possess the highest BET values.

#### 15 WHAT WE CLAIM IS:—

1. A process for the production of finely dispersed precipitated calcium carbonate having a disturbed calcite lattice a loose secondary particle structure, and containing silicic acid in an amount corresponding to an SiO<sub>2</sub> content of 0.1 to 20% by weight calculated on CaCO<sub>3</sub>, which process comprises reacting an aqueous calcium hydroxide suspension of not more than 1.0 molar concentration, at a starting temperature of 10° C. to 30° C., with carbon dioxide in the presence of an added aqueous alkali metal silicate solution or of an added freshly prepared silicic acid solution, the latter containing SiO<sub>2</sub> ions in a low polymerized state and having an SiO<sub>2</sub> content of not more than 10% by weight, and

interrupting the supply of carbon dioxide to the suspension upon reaching a pH value of from 8.5 to 11 therein.

2. A process according to claim 1 wherein the silicic acid solution is prepared by diluting a water-glass solution to the SiO<sub>2</sub> content specified in claim 1, or by acidifying a dilute water-glass solution, or by treating a silicate solution with H<sup>+</sup> exchange resin.

3. A process according to claim 1 or 2 wherein the supply of carbon dioxide is interrupted upon reaching a pH value of from 9 to 10 in the suspension.

4. A process according to claim 1, 2 or 3 wherein the calcium hydroxide suspension contains a water soluble salt of nitrilotriacetic acid in an amount of 0.01 to 0.5% by weight of the calcium hydroxide content of the suspension.

5. Process as claimed in claim 1 substantially as described in any of the foregoing Examples.

6. Calcium carbonate prepared according to any preceding claim.

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